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(54) [Title of the Invention]

POLYESTER-BASED RESIN FOAM MANUFACTURING METHOD AND  
15 FOAMABLE POLYESTER-BASED RESIN MATERIAL MANUFACTURING  
METHOD

(57) [Abstract]

[Problem] A method of manufacturing a resin foam by an  
extremely simple method by which the material is left  
20 to stand at room temperature or heated at a low  
temperature by hot air or the like is provided, and a  
method of manufacturing a foamable polyester-based  
resin material as the material for manufacturing the  
foam is also provided.

25 [Solving Means] A polyester-based resin foam  
manufacturing method is characterized by including  
forming a foamable resin material by impregnating a

foaming resin material, which is made of a resin mainly containing a polyester-based resin having a glass transition temperature (Tg) of 30°C to 80°C, with carbon dioxide at an impregnating temperature which satisfies inequality (1) below, and foaming the foamable resin material at a foaming temperature which satisfies inequality (2) below.

[Mathematical 1]

$$3 \leq \text{impregnating temperature } [^{\circ}\text{C}] \leq -2.2X + 60 \quad (1)$$

[Mathematical 2]

$$(\text{Tg } [^{\circ}\text{C}] - 50) \leq \text{foaming temperature } [^{\circ}\text{C}] \leq \text{Tg } [^{\circ}\text{C}] \quad (2)$$

[where X indicates an impregnation amount (wt%) of carbon dioxide in the foaming resin material]

[What Is Claimed Is:]

[Claim 1]

A polyester-based resin foam manufacturing method characterized by comprising forming a foamable resin material by impregnating a foaming resin material, which is made of a resin mainly containing a polyester-based resin having a glass transition temperature (Tg) of 30°C to 80°C, with carbon dioxide at an impregnating temperature which satisfies inequality (1) below, and foaming the foamable resin material at a foaming temperature which satisfies inequality (2) below.

[Mathematical 1]

$$3 \leq \text{impregnating temperature } [^{\circ}\text{C}] \leq -2.2X + 60 \quad (1)$$

[Mathematical 2]

$$(\text{Tg } [^{\circ}\text{C}] - 50) \leq \text{foaming temperature } [^{\circ}\text{C}] \leq \text{Tg } [^{\circ}\text{C}] \quad (2)$$

[where X indicates an impregnation amount (wt%) of carbon dioxide in the foaming resin material]

[Claim 2]

The polyester-based resin foam manufacturing method according to claim 1, characterized in that the impregnation amount X of carbon dioxide in the foaming resin material is 2.5 to 25 wt%.

[Claim 3]

The polyester-based resin foam manufacturing

method according to claim 1 or 2, characterized in that the foaming resin material has a particulate shape, and particulate polyester-based resin foam is obtained.

[Claim 4]

5           A foamable polyester-based resin material  
manufacturing method characterized by comprising  
impregnating a foaming resin material, which is made of  
a resin mainly containing a polyester-based resin  
having a melt calorie of less than 0.1 J/g (including 0  
10 J/g) measured by differential scanning calorimetry,  
with carbon dioxide at an impregnating temperature  
which satisfies inequality (1) below.

[Mathematical 3]

$$3 \leq \text{impregnating temperature } [^{\circ}\text{C}] \leq -2.2X + 60$$

15 (1)

[where X indicates an impregnation amount (wt%) of carbon dioxide in the foaming resin material]

[Claim 5]

The foamable polyester-based resin material manufacturing method according to claim 4, characterized in that the impregnation amount X of carbon dioxide in the foaming resin material is 2.5 to 25 wt%.

[Claim 6]

25           The foamable polyester-based resin material  
manufacturing method according to claim 4 or 5,  
characterized in that the foaming resin material has a

particulate shape.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Belongs]

5           The present invention relates to a  
polyester-based resin foam manufacturing method and  
foamable polyester-based resin material manufacturing  
method.

[0002]

10   [Prior Art]

As described in Japanese Patent Publication  
No. 56-5333, a general method of manufacturing foamed  
particles made of a resin such as polyethylene or  
polypropylene having a high chemical resistance is ①  
15   a method (to be referred to as a direct foaming method  
hereinafter) in which resin particles and a dispersant  
are stirred in a closed vessel at a high temperature  
and high pressure, the resin particles are impregnated  
with a foaming agent by injecting it into the vessel,  
20   and the resin particles in the vessel and the  
dispersant are discharged from the vessel to a  
low-pressure vessel, thereby forming foamed particles.  
On the other hand, as functional foamed particles other  
than polyethylene and polypropylene foamed particles,  
25   foamed particles made of polyester-based resins such as  
polyethylene terephthalate and polycarbonate are  
beginning to be put into practical use. As a method of

manufacturing foamed particles made of the polyester-based resin, the direct foaming method or ② a method (to be referred to as a strand foaming method hereinafter) by which foamed particles are obtained by cutting strand foam formed by an extrusion foaming machine is known. Also, as a method of manufacturing sheet-like, block-like, or lump-like foam other than particulate foam, ③ an extrusion foaming method using an extruder is generally used although in-situ foaming of an urethane resin at room temperature is put into practical use in some cases. However, any of methods ① to ③ above requires a specially expensive foaming apparatus and large amounts of energy.

[0003]

15 [Problems That the Invention Is to Solve]

Problems, therefore, to be solved by the present invention are to provide a method of manufacturing a resin foam by an extremely simple method by which the material is left to stand at room temperature or heated at a low temperature by hot air or the like, without using the direct foaming method or strand foaming method described above, and a method of manufacturing a foamable polyester-based resin material as the material for manufacturing the foam.

25 [0004]

[Means of Solving the Problems]

The present inventors made extensive studies on

resin foam manufacturing methods in order to solve the above problems, and have found that when carbon dioxide is used as a foaming agent and the relationship between the impregnation amount of this carbon dioxide in a  
5 foaming resin material made of a polyester-based resin and the impregnating temperature of the carbon dioxide satisfies certain conditions, a foamable resin material which readily foams when left to stand at room temperature or heated at a low temperature can be  
10 obtained, thereby achieving the present invention. That is, the present invention provides a polyester-based resin foam manufacturing method and foamable polyester-based resin material manufacturing method presented below.

15 (1) A polyester-based resin foam manufacturing method is characterized by comprising forming a foamable resin material by impregnating a foaming resin material, which is made of a resin mainly containing a polyester-based resin having a glass transition  
20 temperature ( $T_g$ ) of  $30^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , with carbon dioxide at an impregnating temperature which satisfies inequality (1) below, and foaming the foamable resin material at a foaming temperature which satisfies inequality (2) below.

25 [Mathematical 4]

$$3 \leq \text{impregnating temperature } [^{\circ}\text{C}] \leq -2.2X + 60$$

(1)

[Mathematical 5]

$$(T_g [^{\circ}\text{C}] - 50) \leq \text{foaming temperature } [^{\circ}\text{C}] \leq T_g [^{\circ}\text{C}] \quad (2)$$

[where X indicates an impregnation amount (wt%) of  
5 carbon dioxide in the foaming resin material]

(2) The method described in item (1) above is characterized in that the impregnation amount X of carbon dioxide in the foaming resin material is 2.5 to 25 wt%.

10 (3) The method described in item (1) or (2) above is characterized in that the foaming resin material has a particulate shape, and particulate polyester-based resin foam is obtained.

(4) A foamable polyester-based resin material  
15 manufacturing method is characterized by comprising impregnating a foaming resin material, which is made of a resin mainly containing a polyester-based resin having a melt calorie of less than 0.1 J/g (including 0 J/g) measured by differential scanning calorimetry,  
20 with carbon dioxide at an impregnating temperature which satisfies inequality (1) below.

[Mathematical 6]

$$3 \leq \text{impregnating temperature } [^{\circ}\text{C}] \leq -2.2X + 60 \quad (1)$$

25 [where X indicates an impregnation amount (wt%) of carbon dioxide in the foaming resin material]

(5) The method described in item (4) above is



characterized in that the impregnation amount X of carbon dioxide in the foaming resin material is 2.5 to 25 wt%.

(6) The method described in item (4) or (5) above is characterized in that the foaming resin material has a particulate shape.

[0005]

[Embodiment]

A polyester-based foam (to be also simply referred to as a foam hereinafter) in the present invention is manufacturing by foaming a foamable resin material manufactured by using a polyester-based resin as a base resin. In the present invention, a base resin mainly containing a polyester-based resin having a glass transition temperature (Tg) of 30°C to 80°C is used as the foaming resin material. This resin includes a homopolymer, a copolymer, and a mixture of two or more types of resins. Practical examples are aromatic polyester-based resins such as polyethylene terephthalate, a copolymer of terephthalic acid and neopentylglycol isophthalate, and a copolymer of terephthalic acid, ethyleneglycol, and cyclohexanedimethanol, and aliphatic polyester-based resins such as polylactic acid. Note that "mainly containing the polyester-based resin" means that 50 wt% or more of the polyester-based resin is contained in the base resin. Note also that the content of the

polyester-based resin in the base resin is preferably 70 wt% or more, and more preferably 90 wt% or more. In the present invention, a biodegradable polylactic acid resin is favorably used as the polyester-based resin.

5 [0006]

In the present invention, to obtain a foamable resin material which foams at a foaming temperature of preferably 15°C to 50°C, and more preferably 20°C to 40°C, a polyester-based resin having a Tg of preferably 40°C to 80°C, and more preferably 40°C to 70°C need only  
10 be used as the foaming material.

[0007]

In the present invention, a base resin mainly containing polylactic acid is favorably used as the  
15 foaming resin material. This polylactic acid is a polymer which contains 50 wt% or more of a lactic acid component as the weight of a monomer to be polymerized. This polymer includes, e.g., (1) a polymer of lactic acid, (2) a copolymer of lactic acid and another  
20 aliphatic hydroxycarboxylic acid, (3) a copolymer of lactic acid, aliphatic polyvalent alcohol, an aliphatic polyvalent carboxylic acid, (4) a copolymer of lactic acid and another aliphatic polyvalent carboxylic acid, and (5) a mixture obtained by combining any of (1) to  
25 (4) above.

[0008]

In the present invention, when polylactic acid is

to be used as the foaming resin material, biodegradable aliphatic polyester containing at least 35 mol% of an aliphatic ester component can be mixed in the polylactic acid. This aliphatic polyester includes, 5 e.g., a hydroxy acid polycondensate, a ring opening polymer of lactone, and a polycondensate of aliphatic polyvalent alcohol and aliphatic polyvalent carboxylic acid. An example of the hydroxy acid polycondensate is a polycondensate of hydroxybutyric acid. An example of 10 the ring opening polymer of lactone is polycaprolactone. Examples of the polycondensate of aliphatic polyvalent alcohol and aliphatic polyvalent carboxylic acid are polybutylene succinate, polybutylene succinate adipate, and poly(butylene adipate/terephthalate). The mixing 15 amount of the biodegradable aliphatic polyester in the polylactic acid is 50 wt% or less, and preferably 5 to 30 wt% with respect to the total amount of the two materials.

[0009]

20 Practical examples of the polymer of lactic acid are polymers made of L-lactic acid, D-lactic acid, DL-lactic acid, L-lactide, D-lactide, DL-lactide, and a mixture of these materials.

[0010]

25 Practical examples of the method of manufacturing polylactic acid are a method (e.g., a manufacturing method disclosed in U.S. Patent No. 5,310,865) which

directly dehydrates and polycondensates lactic acid or a mixture of lactic acid and aliphatic hydroxycarboxylic acid, a ring opening polymerization method (e.g., a manufacturing method disclosed in 5 U.S. Patent No. 2,758,987) which polymerizes a cyclic dimer (lactide) of lactic acid, a ring opening polymerization method (e.g., a manufacturing method disclosed in U.S. Patent No. 4,057,537) which polymerizes a cyclic dimer of lactic acid and aliphatic 10 hydroxycarboxylic acid, e.g., lactide or glycolide and  $\epsilon$ -caprolactone, in the presence of a catalyst, a method (e.g., a manufacturing method disclosed in U.S. Patent No. 5,428,126) which directly dehydrates and polycondensates a mixture of lactic acid, aliphatic 15 divalent alcohol, and aliphatic dibasic acid, a method (e.g., a manufacturing method disclosed in European Patent No. 0712880 A2) which condensates polylactic acid, aliphatic divalent alcohol, aliphatic dibasic acid, and a polymer in the presence of an organic 20 solvent, and a method which performs solid phase polymerization in at least a predetermined step when a polyester polymer is to be manufactured by dehydrating and polycondensating lactic acid in the presence of a catalyst. However, the manufacturing method is not 25 particularly limited. It is also possible to perform copolymerization in the presence of a small amount of aliphatic polyvalent alcohol such as glycerin,

aliphatic polybasic acid, or polyvalent alcohol such as polysaccharide, or to increase the molecular weight by using a binder (polymer chain extender) such as a polyisocyanate compound.

5 [0011]

To favorably manufacture a foamable resin material in the present invention, a foaming resin material is formed by using the conventionally known method and impregnated with carbon dioxide to obtain a  
10 foamable resin material. Especially when a particulate foaming resin material is to be formed, a base resin is melt-kneaded and extruded into a strand by using an extruder. The strand is cut into an appropriate length after, before, or while it is cooled. Note that when  
15 the foaming resin material is to be formed from a polyester-based resin exhibiting a melting point, the strand is rapidly cooled in the above method such that the exotherm measured by differential scanning calorimetry is 15 J/g or more. This exotherm is based  
20 on the crystallization of the polyester-based resin in a low crystal state or amorphous state during the course of heating in the differential scanning calorimetry.

[0012]

25 The shape of the foaming resin material is preferably a particle because it is possible to fill the obtained foam in a mold and manufacture a foamed

molded product having a relatively free shape by thermally melting the foam, and because the filling properties are favorable when the material is used as a heat insulating material, buffering material, or vibration insulating material for filling.

[0013]

Note that when a particulate foaming resin material is to be formed, if the base resin is hygroscopic in the step of melt-kneading and extruding the base resin into a strand by the extruder, this base resin is preferably dried beforehand. This is so because if a resin containing a large amount of water is charged into the extruder, air bubbles having an adverse effect on the uniformity of foam of foamed particles may be mixed in the foaming resin material, or the physical properties of the base resin may deteriorate to extremely increase the melt flow rate (MFR) when melt kneading is performed in the extruder. To suppress the deterioration of the resin, therefore, it is possible to remove water from the base resin by vacuum suction by using a vented extruder. Also, the extrusion temperature is so set that the MFR of the base resin does not extremely increase. The weight of one particle of the foaming resin material is 0.05 to 10 mg, and preferably 1 to 4 mg. The foaming resin material to be impregnated with carbon dioxide can take various shapes. These shapes include, e.g., bar-like,

plate-like, and lump-like molded products, in addition to particles (pellets).

[0014]

In the present invention, the base resin of the  
5 foaming resin material may also be colored by adding a coloring pigment or dye having a color such as black, gray, brown, blue, or green. A colored foam can be obtained by using a colored resin obtained from a colored base resin. Examples of the colorant are  
10 organic and inorganic pigments and dyes. As these pigments and dyes, various conventionally known materials can be used. Also, an inorganic material such as talc, calcium carbonate, borax, zinc borate, or aluminum hydroxide can be added as a foam adjusting  
15 agent to the base resin in advance. When an additive such as the coloring pigment, dye, or inorganic material is to be added to the base resin, the additive can be directly kneaded in the base resin. When the dispersibility and the like are taken into account,  
20 however, it is normally desirable to form a master batch of the additive and knead this master batch in the base resin. The addition amount of the foam adjusting agent, pigment, or dye is normally preferably 0.001 to 5 parts by weight with respect to 100 parts by  
25 weight of the base resin. In addition, the effect of improving the foaming magnification can be obtained by adding the inorganic material to the base resin.

Furthermore, in the present invention, it is also possible to mix additives such as a fire retardant, antistatic agent, weathering agent, and thickening agent in the base resin.

5 [0015]

Note that high-concentration addition of the additives such as the pigment and foam adjusting agent is undesirable since the product is probably discarded after being used. Also, the obtained foaming resin  
10 material is preferably stored in an environment in which no hydrolysis progresses. Furthermore, the foamable resin material and foam are also preferably stored in a similar environment.

[0016]

15 Although the polyester-based resin used as the base resin in the present invention includes both crystalline and amorphous resins, the use of an amorphous resin is favorable because the cold foamability of the obtained foamable resin material  
20 improves. Also, gelled foamed particles are preferably used in a method by which a particulate foamable resin material is formed by using an amorphous resin, foamed particles are formed by foaming this foamable resin material, and the foamed particles are heated and  
25 molded in a mold. To gel the foamed particles, the amorphous polyester-based resin forming the particles or a resin mainly containing this resin need only be



gelled. The method of gelation includes various conventionally known methods such as a method using an organic peroxide, electron crosslinking method, silane crosslinking method, and polyisocyanate crosslinking method. The gelation ratio of the gelled polyester-based resin used in the present invention is 5% to 100%, preferably 20% to 90%, and more preferably 30% to 80%. In this specification, the melt calorie of the amorphous polyester-based resin is less than 0.1 J/g (including 0 J/g) when measured by differential scanning calorimetry.

[0017]

In the present invention, the foaming resin material is impregnated with carbon dioxide. This carbon dioxide impregnation can be performed in a closed vessel in which carbon dioxide is injected such that the pressure ranges from 5 to 100 kgf/cm<sup>2</sup> G. It is also possible to place the foaming resin material and a dispersant in a closed vessel, inject carbon dioxide within the pressure range described above, and stir the contents while the temperature is adjusted, thereby impregnating the foaming resin material with carbon dioxide. The resin material thus impregnated with carbon dioxide is foamable, and handled as a foamable resin material.

[0018]

When a foamable resin material is to be

manufactured by impregnating the foaming resin material with carbon dioxide, the impregnating temperature of carbon dioxide must be defined in relation to the impregnation amount. In the present invention, the  
 5 impregnating temperature is defined within the range represented by inequality (1) below.

[Mathematical 7]

$$3 \leq \text{impregnating temperature } [^{\circ}\text{C}] \leq -2.2X + 60 \quad (1)$$

10 where X is the carbon dioxide impregnation amount (wt%) in the foaming resin material. The impregnation amount X is represented by equation (3) below.

[Mathematical 8]

$$\text{Impregnation amount X (wt\%)} = A \times 100 / (A + B) \quad (3)$$

15 A: the weight of carbon dioxide with which the foaming resin material is impregnated

B: the weight of the foaming resin material before being impregnated with carbon dioxide

A in the above equation is calculated from the weight  
 20 difference between the foaming resin materials before and after being impregnated with carbon dioxide, and the weight of the foaming resin material can be measured to 0.0001 g.

[0019]

25 In the present invention, if the impregnating temperature is less than 3°C, installation problems may arise during industrial production. Also, besides

problems may arise in the installation for low-temperature carbon dioxide impregnation and in the foamable resin material storage installation, if the foamable resin material impregnated with carbon dioxide at the low temperature is foamed at room temperature, the closed cell ratio of the obtained foam may decrease, or the variation in apparent density may increase. On the other hand, if the impregnating temperature exceeds  $(-2.2X + 60)^{\circ}\text{C}$ , the progress of excess crystallization may make foaming at a foaming temperature of about  $15^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  impossible especially when the foaming resin material is made of a polyester-based resin such as crystalline polylactic acid having an exotherm of 15 J/g or more measured by differential scanning calorimetry. When the foaming resin material is made of an amorphous polyester-based resin, this foaming resin material may soften and largely deform, or particles of the particulate foaming resin material may combine to each other. Note that when a foaming resin material mainly containing a crystalline polyester-based resin is to be impregnated with carbon dioxide, the impregnating temperature is more preferably  $(-2.7X + 55)^{\circ}\text{C}$  or less, and most preferably  $(-3.0X + 55)^{\circ}\text{C}$  or less. In this specification, the impregnating temperature of carbon dioxide when the foamable resin material is to be manufactured by impregnating the foaming resin material

with carbon dioxide is the temperature of a gas in a resin particle ambient if the resin material is to be impregnated with carbon dioxide without using any dispersant in a closed vessel, and is the temperature of a dispersant if the resin material is to be impregnated with carbon dioxide by placing the material together with the dispersant in a closed vessel. In particular, in this specification, the impregnation amount X of carbon dioxide in the foaming resin material is preferably 2.5 to 25 wt%, more preferably 5 to 25 wt%, and most preferably 5 to 17 wt%.

[0020]

Although it depends on the impregnation amount of carbon dioxide, the foamable resin material containing carbon dioxide can be stored, while its foaming capability is maintained, by managing it under low-temperature high-pressure conditions (the temperature is about  $(T_g [^{\circ}\text{C}] - 65)^{\circ}\text{C}$  or less, and the pressure is about 5 to 100 kgf/cm<sup>2</sup> G), and can be foamed by holding it at an appropriate temperature and atmospheric pressure. In the present invention, however, the following temperature range can be advantageously used as the foaming temperature. Note that this foaming temperature is preferably adjusted to be higher than the impregnating temperature.

[Mathematical 9]

$$(T_g [^{\circ}\text{C}] - 50) \leq \text{foaming temperature } [^{\circ}\text{C}] \leq T_g$$

[°C]

(2)

where  $T_g$  indicates the glass transition temperature (°C) of the base resin.

[0021]

5           The foamable resin material can be foamed by conventionally known methods, e.g., a method by which the foamable resin material is filled in a closed vessel and thermally foamed by supplying steam. However, it is possible to preferably use a simple  
10 method using a simple installation in which the foamable resin material is foamed as it is, e.g., left to stand in a temperature-controlled space, left to stand at room temperature, or charged into hot water or room-temperature water. Note that in this  
15 specification, the foaming temperature means the temperature of an ambient gas when the foamable resin material is to be foamed in a gas ambient, and the temperature of a dispersant when the foamable resin material is to be foamed in the dispersant. Note also  
20 that if a heating medium such as air, e.g., warm air or hot air, or steam is to be used, the foaming temperature means the ambient temperature of a space in which this heating medium is supplied. The foaming temperature is normally (glass transition temperature  
25  $T_g$  [°C] - 50 [°C]) to (glass transition temperature  $T_g$  [°C]) of the base resin and, preferably (glass transition temperature [°C] - 40 [°C]) to (glass

transition temperature  $T_g$  [ $^{\circ}\text{C}$ ]). If the foaming temperature is lower than this range, sufficient foaming hardly occurs. If the foaming temperature is higher than this range, the closed cell ratio of the foam decreases, so only the foam inferior in strength can be obtained.

[0022]

In this specification, a polyester-based resin having a glass transition temperature of  $30^{\circ}\text{C}$  to  $80^{\circ}\text{C}$  is used as the base resin. If the glass transition temperature exceeds  $80^{\circ}\text{C}$ , foaming is difficult to perform by a simple method. If the glass transition temperature is less than  $30^{\circ}\text{C}$ , the impregnation amount of carbon dioxide increases, so the lower limit of the foaming temperature range may largely fall below room temperature. This may make density control difficult.

[0023]

In this specification, the base resin melting point ( $T_m$ ) and glass transition temperature ( $T_g$ ) are measured in conformity with JIS K 7121 - 1987. The melting point is the peak temperature of an endothermic peak obtained from a second DSC curve obtained by differential scanning calorimetry. Note that if two or more endothermic peak temperatures appear, the peak temperature of an endothermic peak at the highest temperature is the melting point. The glass transition temperature is an intermediate-point glass transition

temperature between points at which straight lines at equal distances in the ordinate direction from straight lines extended from baselines obtained from a second DSC curve obtained by differential scanning calorimetry intersect a curve of a staircase changing portion of glass transition. The second DSC curve obtained by differential scanning calorimetry of the base resin is a DSC curve obtained by heating 1 to 5 mg of the base resin to 200°C at a heating rate of 10°C/min, cooling the resin from 200°C to 0°C at a cooling rate of 10°C/min, and heating the resin to 200°C at a heating rate of 10°C/min again by using a differential scanning calorimeter. Also, in this specification, the melt calorie (J/g) measured by differential scanning calorimetry is measured in conformity with JIS K 7122 - 1987, and calculated from the endothermic peak area of the second DSC curve obtained by heating 1 to 5 mg of the polyester-based resin to 200°C at a heating rate of 10°C/min, cooling the resin to 0°C at a cooling rate of 10°C/min, and heating the resin to 200°C at a heating rate of 10°C/min again by using a differential scanning calorimeter. Furthermore, in this specification, the exotherm (J/g) obtained by differential scanning calorimetry is measured in conformity with JIS K 7122 - 1987, and calculated from the exothermic peak area of a first DSC curve obtained by heating 1 to 5 mg of the foaming resin material to

200°C at a heating rate of 2°C/min by using a differential scanning calorimeter.

[0024]

The apparent density of the foam obtained by the present invention is preferably 0.015 to 0.3 g/cm<sup>3</sup>, and more preferably 0.015 to 0.2 g/cm<sup>3</sup>. If this density is higher than the above range, the advantage of a light weight obtained by foaming may become unsatisfactory. If the density is lower than the above range, the foaming magnification is relatively high, so the mechanical strength may become insufficient depending on the application. In this specification, the apparent density ( $W1/V1$ ) of the foam is calculated by preparing a measuring cylinder containing ethanol at 23°C, sinking the foam (or a foam group), which is left to stand for two days at a relative humidity of 50%, 23°C, and 1 atm, in the ethanol of the measuring cylinder by using metal gauze or the like, and dividing a weight  $W1$  (g) of the foam (or the foam group) placed in the measuring cylinder by a volume  $V1$  (cm<sup>3</sup>) of the foam (or the foam group) read from the rise of the level of the ethanol. Note that if the foam is too large to be sunk in the ethanol of the measuring cylinder, the foam is cut and used as a measurement specimen.

[0025]

Also, in this specification, the gelation ratio



(%) is measured as follows. That is, the gelation ratio of the foam or foamable resin material is measured as follows. About 1 g of the foam or foamable resin material is used as a sample to measure a sample weight W2. The weighed sample and 100 ml of chloroform are placed in a 150-ml flask, and refluxed under heating at an atmospheric pressure and 62°C for 10 hrs. After that, while the obtained heated product is sufficiently hot, i.e., at 50°C or more, it is filtered by using a suction filtering apparatus having 200-mesh metal gauze. The obtained filtered product on the metal gauze is dried in an oven at 80°C and 30 to 40 Torr for 8 hrs. A weight W1 of the obtained dried product is measured. The percentage  $(W1/W2) \times 100$  of the weight ratio of the weight W1 to the sample weight W2 is the gelation ratio.

[0026]

[Examples]

[0027]

Examples 1 & 2

Amorphous polylactic acid (LACTY9800 manufactured by Shimadzu), talc, and a polyisocyanate compound (MILLIONATE MR-200: manufactured by NIPPON POLYURETHANE INDUSTRY) were melt-kneaded at a cylinder temperature of 180°C and extruded into a strand by using a biaxial extruder. Then, the strand was rapidly cooled and set in water at about 20°C, and cut to obtain foaming resin

particles (a particulate foaming resin material) having a diameter of about 1.3 mm, a length of about 1.9 mm, and a weight of about 3 mg. Note that the addition amounts of talc and polyisocyanate compound were 1 and 5 3 wt%, respectively. Note also that the compound name of the polyisocyanate compound is "polymethylene polyphenyl polyisocyanate".

[0028]

The obtained resin particles were stored in an ambient at about 30°C and a relative humidity of about 10 50% for 14 days. After an autoclave having a volume of 5 L was adjusted to 10°C, 1,000 g of the resin particles were charged into this autoclave. Carbon dioxide gas was injected into the autoclave via a pressure adjusting valve to adjust the internal 15 pressure of the autoclave to 4 MPa, and the pressure was held for 15 hrs. Then, the carbon dioxide gas in the autoclave was exhausted, and the foamable resin particles (the particulate foamable resin material) 20 were removed. The carbon dioxide gas impregnation amount in the foaming resin particles was 20 wt%. The resin particles thus impregnated with the carbon dioxide gas were expanded and foamed by holding them in an environment at a foaming temperature shown in Table 1. Table 1 shows the apparent density and gelation 25 ratio of the obtained foamed particles (the particulate foam).

[0029]

Examples 3 & Comparative Example 1

Crystalline polylactic acid (LACTY9030  
manufactured by Shimadzu) and talc were melt-kneaded  
5 and extruded into a strand by using an extruder. Then,  
the strand was rapidly cooled and set in water at about  
25°C, and cut to obtain foaming resin particles (a  
particulate foaming resin material) having a diameter  
of about 1.3 mm, a length of about 1.9 mm, and a weight  
10 of about 3 mg. Note that the addition amount of talc  
was 2,000 ppm. After an autoclave having a volume of 5  
L was adjusted to an ambient temperature shown in Table  
1, 1,000 g of the resin particles were charged into  
this autoclave. Carbon dioxide gas was injected into  
15 the autoclave via a pressure adjusting valve to adjust  
the internal pressure of the autoclave to a pressure  
shown in Table 1, and the pressure was held for 15 hrs.  
Then, the carbon dioxide gas in the autoclave was  
exhausted, and the foamable resin particles (the  
20 particulate foamable resin material) were removed.  
Note that in Comparative Example 1, the resin particles  
were first cooled to 20°C and then removed. The carbon  
dioxide gas impregnation amount in the foaming resin  
particles was as shown in Table 1.

25 [0030]

The resin particles thus impregnated with the  
carbon dioxide gas were charged into a closed vessel,

and heated at a foaming temperature shown in Table 1 by supplying steam, thereby obtaining expanded and foamed particles (particulate foam). Table 1 shows the apparent density and gelation ratio of the obtained

5 foamed particles.

[0031]

[Table 1]

No.	Base Resin				Foaming Resin Particles	CO <sub>2</sub> Impregnating Conditions	
	Type	Tg (°C)	Tm (°C)	Melt Calorie (I/g)	Exotherm (I/g)	Temperature (°C)	Pressure (MPa)
Example 1	Polylactic acid	53	-	0	0	10	4
Example 2	Polylactic acid	53	-	0	0	10	4
Example 3	Polylactic acid	60	149	10	30	10	2
Comparative Example 1	Polylactic acid	60	149	10	30	50	3

No.	CO <sub>2</sub> Impregnation Amount (wt%)	Foaming Temperature (°C) and Heating Method	Foamed Particle Apparent Density (g/cm <sup>3</sup> )	Gelation Ratio (%)
Example 1	20	15/atmosphere	0.134	40
Example 2	20	25/water	0.078	40
Example 3	7.8	45/steam	0.160	less than 1
Comparative Example 1	8.1	45/steam	0.980	less than 1

Table 2 shows the relationship between the CO<sub>2</sub> impregnation amount (X), the impregnating temperature, and the value of  $-2.2X + 60$  in the examples and comparative example.

5 [Table 2]

	CO <sub>2</sub> Impregnation Amount: X (wt%)	Impregnating Temperature (°C)	$-2.2X+60(°C)$
Example 1	20	10	16
Example 2	20	10	16
Example 3	7.8	10	42.8
Comparative Example 1	8.1	50	42.2

[0032]

[Effects of the Invention]

The present invention provides a foamable resin material which can be well foamed by an extremely simple method by which the material is left to stand at room temperature or heated at a low temperature by hot air or the like, and a foam manufacturing method using the same. The foam obtained by the present invention has favorable buffering properties and high mechanical strength, and can be preferably used as, e.g., a filling material, buffering material, packaging material, sound absorbing material, or vibration insulating material. Especially when a biodegradable resin such as polylactic acid is selected as the polyester-based resin, the biodegradability facilitates the waste disposal of the foam after it is used. That is, the foam has a number of industrial advantages. Also, particularly a particulate foamable resin material and particulate foam improve the filling properties when the foamable resin material is used as a filling material, and the foam can be molded in a mold.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 shows a DSC curve for calculating the exotherm of foaming resin particles used in Examples 1 and 2.

[Fig. 2]

Fig. 2 shows a DSC curve for calculating the exotherm

of foaming resin particles used in Example 3 and Comparative Example 1.

[Fig. 3]

Fig. 3 shows a DSC curve for calculating the melt  
5 calorie of a base resin used in Examples 1 and 2.

[Fig. 4]

Fig. 4 shows a DSC curve for calculating the melt  
calorie of a base resin used in Example 3 and  
Comparative Example 1.

10

FIG. 1

(1): EXOTHERM

(2): TEMPERATURE

(3): NO EXOTHERMIC PEAK

5

FIG. 2

(1): EXOTHERMIC PEAK FOR CALCULATING EXOTHERM

FIG. 3

10 (1): ENDOTHERM

(2): TEMPERATURE

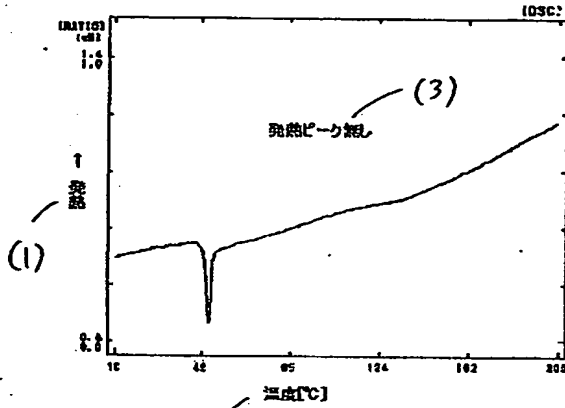
(3): NO ENDOTHERMIC PEAK FOR CALCULATING MELT CALORIE

FIG. 4

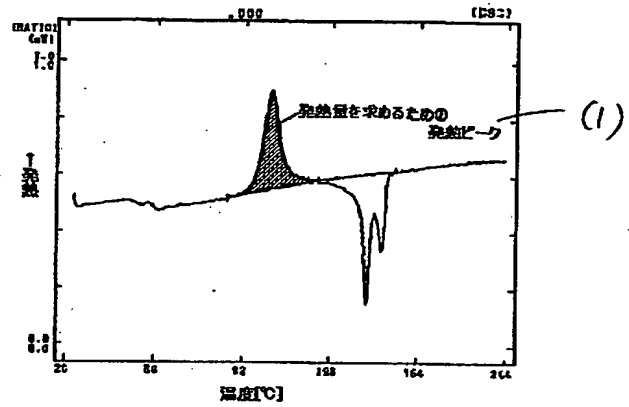
15 (1): ENDOTHERMIC PEAK FOR CALCULATING MELT CALORIE



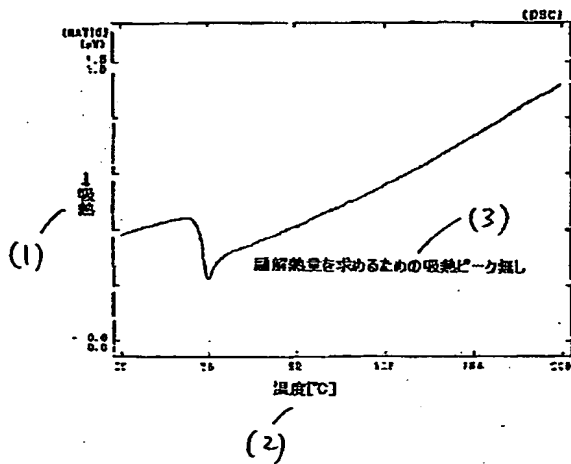
【図1】 Fig. 1



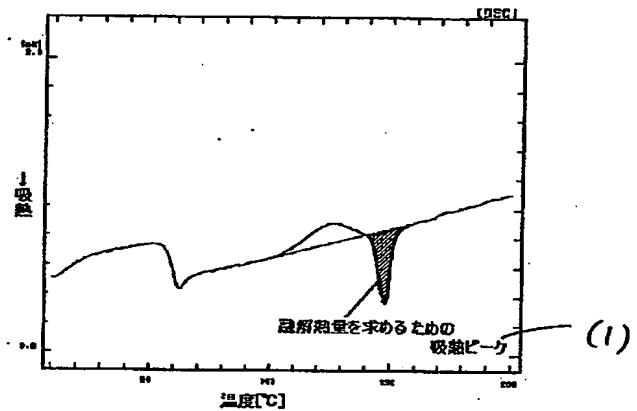
【図2】 Fig. 2



【図3】 Fig. 3



【図4】 Fig. 4



フロントページの続き

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